

## **Appendix D**

### **Supplemental Exposure Assessment Information**

## Technical Memorandum RE: Modeling Worker Inhalation Exposure

## **D.1 Technical Memorandum RE: Modeling Worker Inhalation Exposure**

### **TECHNICAL MEMORANDUM**

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RE: **MODELING WORKER INHALATION EXPOSURE**

#### **I. INTRODUCTION**

This technical memorandum is submitted for review by the RM2 work group. Air transport models to estimate worker inhalation exposure to chemicals from printed wiring board (PWB) making holes conductive (MHC) lines are presented here for review and comment. The purpose is to reach agreement on our technical approach before proceeding with further analysis.

Three air transport models will be required to estimate worker exposure:

- ! Volatilization of chemicals induced by air sparging.
- ! Aerosol generation induced by air sparging.
- ! Volatilization of chemicals from the open surface of MHC tanks.

The total transport of chemicals from the air-sparged baths will be determined by summing the releases calculated using each of the three models described above. Air-sparged baths include the electroless-copper baths and some cleaning tanks. Only the third model will be applied to determine the atmospheric releases of chemicals from unsparged baths. This document includes a review of the relevant literature, descriptions of the models, and examples demonstrating the proposed use of the models. The results of the model calculations will be compared to available occupational monitoring data.

## II. VOLATILIZATION OF CHEMICALS FROM AIR-SPARGED PWB MANUFACTURING TANKS

Mixing in plating tanks, e.g., the electroless copper plating tank, is commonly accomplished by sparging the tank with air. This is similar to aeration in wastewater treatment plants, and the volatilization of chemicals from these plants has been the focus of recent research. The volatilization models used in that research are based on well accepted gas transfer theory, discussed below.

### Background

Volatilization of chemicals from water to air has been investigated by many researchers (Liss and Slater, 1974; Smith *et al.*, 1980; Roberts, 1983; Peng *et al.*, 1993). In PWB manufacturing, volatilization due to air sparging of process tanks is expected to be one of the main pathways for contaminant transfer to the air. In bubble aeration systems, the volatilization rate is dependent upon the volumetric gas flow rate, partial pressure of the gas, and the mass transfer rate coefficient (Matter-Müller, 1981). The volatilization characteristics for different diffuser types and turbulent conditions were evaluated by Matter-Müller (1981), Peng (1995), and Hsieh (1994).

Volatilization from aerated systems has been mainly quantified using the two-film theory (Cohen *et al.*, 1978; Mackay and Leinonen, 1975). This work is discussed below and is used to model chemical transfer rates from air-sparged PWB process tanks. The main assumption of the theory is that the velocity at a fluid interface is zero. Molecular diffusion across the interfacial liquid film is the limiting factor for mass transfer to the air, and it is used to develop a simple equation relating the overall mass transfer coefficient to the diffusion coefficient of the chemical in water.

The two-film model of gas transfer was expanded to include mass transfer in diffused aeration systems (Matter-Müller *et al.*, 1981). Matter-Müller *et al.* assumed that the system was isothermal, hydraulic conditions were steady, and that pressure and volume changes within the bubbles were negligible. Further, an overall mass transfer coefficient was applied to represent transfer of contaminants to the bubble as they rose through the homogeneous liquid volume. Parker (1993) demonstrated that liquid-phase concentration can be assumed constant during the rise time of the bubble. Under these assumptions, Matter-Müller *et al.* derived the following relationship predicting the mass transfer rate from an aerated system:

$$F_{y,s} = Q_G H_y c_{L,y} \left[ 1 - \exp \left( - \frac{K_{OL,y} a V_L}{H_y Q_G} \right) \right] \quad (1)$$

where:

- $F_{y,s}$  = mass transfer rate of chemical y out of the system by sparging (m/t)
- $Q_G$  = gas flow rate (l<sup>3</sup>/t)
- $H_y$  = dimensionless Henry's constant for chemical y
- $c_{L,y}$  = concentration of chemical y in bulk liquid (m/l<sup>3</sup>)
- $K_{OL,y}$  = overall mass transfer coefficient for chemical y (l/t)

$a$  = interfacial area of bubble per unit volume of liquid ( $l^2/l^3$ )  
 $V_L$  = volume of liquid ( $l^3$ )

The overall mass-transfer coefficient is defined as the inverse sum of the reciprocals of the liquid and gas-phase mass transfer coefficients; but, because molecular diffusion of oxygen and nonpolar organic substances is  $10^3$  times greater in air than in water (Matter-Müller *et al.*, 1981), it is set equal to the liquid phase coefficient only. The mass transfer coefficient of a chemical can then be related to oxygen using the following equation:

$$K_{OL,y} = \left( \frac{D_y}{D_{O_2}} \right) K_{OL,O_2} \quad (2)$$

where:

$D_y$  = molecular diffusion coefficient for chemical y in water ( $l^2/t$ )  
 $D_{O_2}$  = molecular diffusion coefficient for oxygen in water ( $l^2/t$ )  
 $= 2.1 \times 10^{-5} \text{ cm}^2/\text{cm} @ 25^\circ \text{C}$  (Cussler, 1984)  
 $K_{OL,y}$  = overall mass transfer coefficient for chemical y ( $l/t$ )  
 $K_{OL,O_2}$  = overall mass transfer coefficient for oxygen in water ( $l/t$ )

The value of  $K_{OL,O_2}$  at  $25^\circ\text{C}$  in diffused aeration systems can be estimated using a correlation developed by Bailey and Ollis (1977):

$$K_{OL,O_2} = 0.31 * \left( \frac{d_b^3 (\rho_{H_2O} - \rho_{air}) g}{\mu_{H_2O} D_{O_2}} \right)^{1/3} \frac{D_{O_2}}{d_b} \quad (3)$$

where:

$d_b$  = bubble diameter ( $l$ )  
 $\rho_{H_2O}$  = density of water ( $m/l^3$ )  
 $\rho_{air}$  = density of air ( $m/l^3$ )  
 $g$  = gravitational constant ( $l/t^2$ )  
 $\mu_{H_2O}$  = viscosity of water ( $m/l \cdot t$ )

If a measured value of  $D_y$  is not available, then it can be calculated from the Hayduk and Laudie correlation (Lyman *et al.*, 1982):

$$D_y (\text{cm}^2/\text{sec}) = \frac{13.26 \times 10^{-5}}{\mu_{H_2O}^{1.14} V_m^{0.589}} \quad (4)$$

where:

$V_m$  = molar volume of solute ( $\text{cm}^3/\text{mol}$ )  
 $\mu_{H_2O}$  = viscosity of water (centipoise)

The mass transfer coefficient can be corrected for the bath temperature (°C) as follows (Tschabanoglous, 1991):

$$K_{OL,y,T} = K_{OL,y,25^{\circ}C} 1.024^{(T-25)} \quad (5)$$

Bailey and Ollis (1977) developed a relationship for the interfacial area per unit volume ( $a$ ) as a function of the bubble diameter, gas flow rate, and tank geometry:

$$a = \frac{6 Q_G t_b}{V_L d_b} \quad (6)$$

where:

$h$  = tank depth (l); and

$$t_b = \frac{18 h \mu_{H_2O}}{d_b^2 (\rho_{H_2O} - \rho_{air})g} \quad (7)$$

Values of  $H_y$  are often reported at 25°C. The Henry's constant can be corrected to the bath temperature using the van't Hoff equation:

$$H_{y,T} = H_{y,25^{\circ}C} \exp \left[ \frac{\Delta H_{gas} - \Delta H_{aq}}{R} \left( \frac{1}{298.15} - \frac{1}{273.15 + T} \right) \right] \quad (8)$$

where:

$\Delta \eta_{gas}$  = enthalpy of the chemical in the gas phase (cal/mol)  
 $\Delta H_{aq}$  = enthalpy of the chemical in the aqueous phase (cal/mol)  
 $R$  = gas constant (1.987 cal/mol·K)

Matter-Müller (1981) concluded that surfactants do not significantly alter the rate of volatilization from the water. Some agents did lower the overall mass transfer coefficient, but most showed no appreciable difference. This was attributed to an increase in the specific interfacial area,  $a$ , when the interfacial energy, or mass transfer coefficient, was decreased. The transfer rate of volatile organic compounds (VOCs) was found to depend heavily upon the type of aerators used, and the degree of saturation of the bubbles rising through the liquid.

### III. AEROSOL GENERATION FROM BATHS MIXED BY SPARGING WITH AIR

Aerosols or mists have been identified as a major source of contaminants released by electroplating baths to the atmosphere (Burgess, 1981) and should be investigated as a potential source of contaminants from electroless baths. At least two sources of aerosols exist in electroplating baths: 1) aerosols generated due to liquid dripping from parts as they are removed

from the bath (drag-out drips); and 2) aerosols generated due to bursting of the bubbles at the surface. Drag-out drips are insignificant compared to other sources of aerosols (Berglund and Lindh, 1987; Cooper et al., 1993).

Bubbles in electroplating baths can originate from the dissociation of water at the electrode, or mixing of the bath via air sparging. Bubbles in other plating baths (e.g., electroless plating baths) can originate from reactions in the bath or mixing of the bath via air sparging. The rate of aerosol generation per unit bubble volume decreases with increasing bubble size. Bubbles generated by water dissociation are typically smaller than those generated by air sparging; therefore, aerosol generation in electroless plating processes may be less significant than in electroplating operations. The focus of this memo is aerosols generated by air sparging. Except for the conductive polymer and non-formaldehyde electroless alternatives, MHC processes in PWB manufacturing do not use electroplating and therefore would not dissociate water to form gas bubbles. Information collection is continuing to allow prediction of aerosol formation in MHC processes that do have an electroplating step. Importantly, Berglund and Lindh (1987) report that aerosol generation from electroplating tanks is greatly reduced by sparging; the relatively large air bubbles formed during air sparging coalesce the smaller bubbles formed by hydrolysis and electroless plating reactions.

To estimate the emission of contaminants resulting from aerosols, the rate of aerosol generation and the concentration of contaminant in the aerosol are required. Limited information concerning the rate of aerosol formation was found in the literature. The following sources were consulted:

- ! U.S. EPA (1991). *Chemical Engineering Branch Manual for the Preparation of Engineering Assessments*.
- ! Chemical Abstracts, 1986 to date.
- ! Current and past text books in air pollution, chemical engineering, and water and wastewater treatment.
- ! Perry's Handbook (1984) related to entrainment in distillation trays.
- ! The last five years of *Water Environment Research* and *ASCE Journal of the Environmental Engineering Division*.
- ! A title key-word search of holdings in the library of the University of Tennessee.
- ! The ASPEN model commonly used for modeling chemical manufacturing processes. (It was found that any aerosol formation routines within ASPEN would be relevant to entrainment in devices such as distillation trays and not relevant to sparging of tanks.)
- ! The manager of the US EPA Center for Environmental Assessment Modeling in Athens, Georgia, as well as an expert in the Air and Energy Lab - Emission Modeling Branch in North Carolina.

In this work, the aerosol formation rates will be predicted based upon limited measurements of aerosol generation in electroplating (Berglund and Lindh, 1987) and other air-sparged baths (Wangwongwatana et al., 1988; Wangwongwatana et al., 1990) found in the literature.

Berglund and Lindh (1987) developed several graphs relating aerosol generation to air sparging rate (Figure 1a), bath temperature (Figure 1b), air flow rate above the bath (Figure 1c), and distance between bath surface and the tank rim (Figure 1d). Using Figures 1a-1d, the following relationship may be developed:

$$R_A = \left[ 5.5 \times 10^{-5} (Q_G / A) + 0.01 \right] F_T F_A F_D \quad (9)$$

where:

- $R_A$  = aerosol generation rate (ml/min/m<sup>2</sup>)
- $Q_G/A$  = air sparging rate per unit bath area (l/min/m<sup>2</sup>)
- $F_T$  = temperature correction factor
- $F_A$  = air velocity correction factor
- $F_D$  = distance between the bath surface and tank rim correction factor

Wangwongwatana et al. (1988) presented figures relating the number of aerosol droplets generated as a function of air flow rate, bubble rise distance, bubble size, and colloid concentration (Figure 2). Droplet size distribution measurements by these researchers indicate volume mean diameters of 5 to 10 µm. The aerosol generation rate can be calculated using the following equation:

$$R_A = \frac{Q_G C_d V_d}{A} \quad (10)$$

where:

- $C_d$  = droplet concentration (l<sup>-3</sup>)
- $V_d$  = droplet volume (l)
- $A$  = bath area (l<sup>2</sup>)

Contaminants may be present in aerosols at elevated concentration relative to the bath concentration. Colloidal contaminants may be collected on the bubble surface as it rises through the bath. As the bubble bursts, the contaminants on the bubble surface are incorporated into aerosols. Wangwongwatana et al. (1990) report that in their experiments about one in two aerosols contain polystyrene latex spheres, compared to about one in 250 expected based upon the concentration of latex sphere in the bath. Organic contaminants may also partition at the air-water interface. A correlation for the water-interface partitioning coefficient for nonpolar compounds,  $k_{IW}$ , defined as the ratio of the mass of contaminant per unit area of interface to the mass of contaminant per unit volume of water is given by Hoff et al. (1993):

$$\log k_{IW} = -8.58 - 0.769 \log C_W^S \quad (11)$$



where:

$C_w^s$  = saturated aqueous solubility of the contaminant.

For more polar compounds a more complicated relationship is required:

$$\log k_{IW} = -7.508 + \log \gamma_w + a_s (\sigma_{wa} - \sigma_{sa} - 1.35 \sigma_{sw}) / 2.303 RT \quad (12)$$

where:

$\gamma_w$  = activity coefficient of the contaminant in water (dimensionless)

$a_s$  = molar area of the solute ( $\text{cm}^2/\text{mol}$ )

$R$  = gas constant ( $8.314 \times 10^7 \text{ erg/mol K}$ )

$F_{WA}$  = surface tension of the water-air interface (dyne/cm)

$F_{SA}$  = surface tension of the solute-air interface (dyne/cm)

$F_{SW}$  = surface tension of the solute-water interface (dyne/cm)

Hoff et al. (1993) also present a relationship for the ratio of the mass of contaminant sorbed at the air-water interface to the mass of contaminant in the gas volume of the bubble:

$$\frac{M_I}{M_b} = \frac{k_{IW}}{H_y (d_b / 6)} \quad (13)$$

where:

$M_I$  = mass of contaminant at the interface

$M_b$  = mass of contaminant in gas bubble

Only a small fraction of the bubble interface will be ejected as aerosols. It may be calculated from the following equation:

$$f_{IE} = \frac{R_A A d_b}{6 Q_G l_b} \quad (14)$$

where:

$f_{IE}$  = fraction of bubble interface ejected as aerosols (dimensionless)

$l_b$  = thickness of bubble film (l)

The rate of mass transfer from the tank to the atmosphere by aerosols,  $F_{y,a}$  (m/t) is given by:

$$F_{y,a} = \frac{M_I}{M_b} f_{IE} F_{y,s} \quad (15)$$

#### IV. VOLATILIZATION OF CHEMICALS FROM THE OPEN SURFACE OF MHC TANKS

Most plating tanks have a free liquid surface from which chemicals can volatilize into the workplace air. Air currents across the tank will accelerate the rate of volatilization. The model presented in the Chemical Engineering Branch Manual for the Preparation of Engineering Assessments (CEBMPEA) (US EPA, 1991) has potential application in this case. Some limitations of the model should be pointed out. The model was developed to predict the rate of volatilization of pure chemicals, not aqueous solutions. The model was also validated using pure chemicals. As a result, the model implicitly assumes that mass transfer resistance on the gas side is limiting. The model may fail in describing volatilization of chemicals from solutions when liquid-side mass transfer controls.

CEBMPEA models the evaporation of chemicals from open surfaces using the following model:

$$F_{y,o} = 2 c_{L,y} H_y A [D_{y,air} v_z / (\pi z)]^{0.5} \quad (16)$$

where:

- $F_{y,o}$  = volatilization rate of chemical y from open tanks (m/t)
- $D_{y,air}$  = molecular diffusion coefficient of chemical y in air (l<sup>2</sup>/t)
- $v_z$  = air velocity (l/t)
- $z$  = distance along the pool surface (l)

The value of  $v_z$  recommended by CEBMPEA is 100 ft·min<sup>-1</sup>. The value of  $D_{y,air}$  can be estimated by the following formula (US EPA, 1991):

$$D_{y,air} = 4.09 \times 10^{-5} T^{1.9} (1/29 + 1/M)^{0.5} M^{-0.33} / P_t \quad (17)$$

where:

- $D_{y,air}$  = molecular diffusion coefficient of chemical y in air (cm<sup>2</sup>/s)
- $T$  = air temperature (K)
- $M$  = molecular weight (g/mol)
- $P_t$  = total pressure (atm)

This equation is based on kinetic theory and generally gives values of  $D_{y,air}$  that agree closely with experimental data.

#### V. CALCULATION OF CHEMICAL CONCENTRATION IN WORKPLACE AIR FROM EMISSION RATES

The indoor air concentration will be estimated from the following equation (US EPA, 1991):

$$C_y = F_{y,T} / (V_R R_V k) \quad (18)$$

where:

$C_y$	= workplace contaminant concentration ( $\text{m}/\text{l}^3$ )
$F_{y,T}$	= total emission rate of chemical from all sources ( $\text{m}/\text{t}$ )
$V_R$	= room volume ( $\text{l}^3/\text{t}$ )
$R_V$	= room ventilation rate ( $\text{t}^{-1}$ )
$k$	= dimensionless mixing factor

The mixing factor accounts for slow and incomplete mixing of ventilation air with room air. CEBMPEA sets this factor to 0.5 for the typical case and 0.1 for the worst case. CEBMPEA commonly uses values of the ventilation rate  $Q$  from  $500 \text{ ft}^3/\text{min}$  to  $3,500 \text{ ft}^3/\text{min}$ . Appropriate ventilation rates for MHC lines will be chosen from facility data and typical industrial recommendations.

## **VI. EXAMPLE MODELING OF FORMALDEHYDE RELEASE TO ATMOSPHERE FROM AIR-SPARGED ELECTROLESS COPPER BATH**

In the examples below, the values of some parameters are based upon a site visit to SM Corporation in Asheville, NC. Except where stated otherwise, final values of the various parameters used in the models will be chosen based on the results of the Workplace Practices Questionnaire, chemical suppliers information, site visits, and performance demonstrations. All parameter values are based on preliminary information and are subject to change.

### **Values of site-specific parameters assumed in the example**

Tank volume = 242 L	Site visit to SM Co., Asheville, NC
Tank depth = 71 cm	Assumed
Tank width = 48 cm	Assumed
Tank length = 71 cm	Assumed
Air sparging rate = 53.80 L/min	Midpoint of values given in Perry's Handbook, 1985, pg 19.13
Tank temperature = 51.67°C	Site visit to SM Co., Asheville, NC
H <sub>2</sub> CO Concentration in tank = 7,000 mg/L	Product data sheets
Bubble diameter at tank surface = 2.00 mm	Assumed
Room length = 20 m	Assumed
Room width = 20 m	Assumed
Room height = 5 m	Assumed
Air turnovers/hour = 4 hr <sup>-1</sup>	Assumed
Air velocity across tank surface = 0.508 m/s	Default recommended by US EPA, 1991
Dimensionless mixing factor = 0.5	Default recommended by US EPA, 1991

### **Volatilization induced by air sparging**

*Calculating overall mass transfer coefficient for oxygen in water:*

$$K_{OL,O_2} = 0.31 * \left( \frac{d_b^3 (\rho_{H_2O} - \rho_{air}) g}{\mu_{H_2O} D_{O_2}} \right)^{1/3} \frac{D_{O_2}}{d_b}$$

$$= 0.0113 \text{ cm/sec}$$

$$= 0.678 \text{ cm/min}$$

where:

$$d_b = 0.2 \text{ cm}$$

$$\rho_{H_2O} = 0.997 \text{ g/cm}^3 \text{ (Dean, 1985)}$$

$$\rho_{gas} = 0.00118 \text{ g/cm}^3 \text{ (Dean, 1985)}$$

$$g = 980 \text{ cm/sec}^2$$

$$\mu_{H_2O} = 0.0089 \text{ (g/cm}\cdot\text{sec) (Dean, 1985)}$$

$$D_{O_2} = 2.1 \times 10^{-5} \text{ cm}^2/\text{sec (Cussler, 1984)}$$

*Calculating molecular diffusion coefficient of formaldehyde in water:*

$$D_y = \frac{13.26 \times 10^{-5}}{\mu_{H_2O}^{1.14} V_m^{0.589}}$$

$$= 1.81 \times 10^{-5} \text{ cm}^2/\text{sec}$$

where:

$$V_m = 36.8 \text{ cm}^3/\text{mol}$$

$$\mu_{H_2O} = 0.89 \text{ centipoise}$$

*Calculating mass transfer coefficient of formaldehyde in water:*

$$K_{OL,y} = \left( \frac{D_y}{D_{O_2}} \right) K_{OL,O_2} = \left( \frac{1.81 \times 10^{-5}}{2.10 \times 10^{-5}} \right) * 0.678$$

$$= 0.584 \text{ cm/min}$$

*Correcting mass transfer coefficient for temperature:*

$$K_{OL,y, 51.67} = K_{OL,y, 25} \cdot 1.024^{(T-25)} = 0.584 * 1.024^{(51.67-25)} = 1.10 \text{ cm/min}$$

*Calculating  $t_b$ :*

$$t_b = \frac{18 \text{ h } \mu_{H_2O}}{d_b^2 (\rho_{H_2O} - \rho_{air}) g}$$

$$= 0.291 \text{ sec}$$

$$= 4.85 \times 10^{-3} \text{ min}$$

where:

$$h = 71 \text{ cm}$$

*Calculating interfacial area per unit volume:*

$$a = \frac{6 Q_G t_b}{V_L d_b} = 0.0323 \text{ cm}^2/\text{cm}^3$$

where:

$$\begin{aligned} Q_G &= 53,800 \text{ cm}^3/\text{min} \\ V_L &= 242,000 \text{ cm}^3 \end{aligned}$$

*Correcting Henry's constant for temperature:*

$$\begin{aligned} H_{y,51.67} &= H_{y,25^\circ\text{C}} \exp \left[ \frac{\Delta H_{\text{gas}} - \Delta H_{\text{aq}}}{R} \left( \frac{1}{298.15} - \frac{1}{273.15 + T} \right) \right] \\ &= 1.99 \times 10^{-5} \text{ (dimensionless)} \end{aligned}$$

where:

$$\begin{aligned} H_{y,25^\circ\text{C}} &= 1.7 \times 10^{-7} \text{ atm} \cdot \text{m}^3/\text{mol} \text{ (Risk Assistant, 1995)} \\ &= 6.38 \times 10^{-6} \text{ (dimensionless)} \\ \text{DH}_{\text{gas}} &= -27,700 \text{ cal/mol} \\ \text{DH}_{\text{aq}} &= -35,900 \text{ cal/mol} \\ R &= 1.987 \text{ cal/mol} \cdot \text{K} \end{aligned}$$

*Calculating mass transfer rate of formaldehyde by air sparging:*

$$\begin{aligned} F_{y,v} &= Q_G H_y c_{L,y} \left[ 1 - \exp \left( - \frac{K_{OL,y} a V_L}{H_y Q_G} \right) \right] \\ &= 7.49 \text{ mg/min} \end{aligned}$$

The argument of the exponential function is -8031. This indicates that the formaldehyde concentration in the air bubbles is essentially in equilibrium with the bath concentration.

## Transport in aerosols

The aerosol generation rate will be estimated using data presented by both Berglund and Lindh (1987) and Wangwongwatana et al. (1988).

*Calculating aerosol generation rate using Berglund and Lindh (1987) data:*

$$R_A = \left[ 5.5 \times 10^{-5} (Q_G/A) + 0.01 \right] F_T F_A F_D$$

$$= 0.0187 \text{ mL/min/m}^2$$

where:

$$Q_G/A = (53.8 \times 10,000)/(71 \times 48) = 158 \text{ (L/min/m}^2\text{)}$$

$$F_T = 0.95 \text{ @ } 51.67^\circ\text{C (Figure 1b)}$$

$$F_A = 1.2 \text{ @ } 0.508 \text{ m/s (Figure 1c)}$$

$$F_D = 1.0 \text{ assumed (Figure 1d)}$$

*Calculating aerosol generation rate using Wangwongwatana et al. (1988) data:*

The air sparging rate used in the example (53.8 L/min) must be converted to an equivalent rate in the experimental apparatus using the ratio of the area of the example bath (0.341 m<sup>2</sup>) to the area of the experimental apparatus (0.123 m<sup>2</sup>). The equivalent rate is 19.4 L/min. The bubble rise distance would be approximately 0.6 m. From Figure 2, it can be inferred that the droplet concentration is not much greater than 100 droplets/cm<sup>3</sup>. The aerosol generation rate can now be calculated:

$$R_A = \frac{Q_G C_d V_d}{A}$$

$$= 8.27 \times 10^{-3} \text{ ml/m}^2\text{/min}$$

where:

$$Q_G = 53800 \text{ cm}^3\text{/min}$$

$$C_d = 100 \text{ droplets/cm}^3$$

$$V_d = (\pi/6) d_d^3 = 5.24 \times 10^{-10} \text{ cm}^3$$

$$d_d = 0.001 \text{ cm (upper end of range reported by Wangwongwatana et al., 1988)}$$

$$A = 0.341 \text{ m}^2$$

The aerosol generation rates calculated by the two methods agree quite well. The model of Berglund and Lindh (1987) will be used because it gives a slightly greater generation rate and is easier to use.

Emission rate from bath. If it is assumed that the formaldehyde concentration in the aerosols is equal to the bath concentration (7 mg/mL) then the formaldehyde emission rate is:

$$F_{y,a} = (7 \text{ mg/mL}) \cdot (0.0187 \text{ mL/m}^2\text{/min}) \cdot (0.341 \text{ m}^2) = 4.46 \times 10^{-2} \text{ mg/min}$$

To determine if accumulation of the contaminant at the air-water interface is significant,  $k_{IW}$  must be estimated using Equation 11. Since formaldehyde is a gas at the temperatures of interest, interfacial tension data are not available; however, average values of other aldehydes may be used (Hoff et al., 1993). Calculation of  $k_{IW}$  @ 25°C is summarized below; information was not available for calculating  $k_{IW}$  at other temperatures.

$$\log k_{IW} = -7.508 + \log \gamma_w + a_s(\sigma_{wa} - \sigma_{sa} - 1.35\sigma_{sw}) / 2.303RT$$

$$= -6.848$$

where:

$$\begin{aligned}\gamma_w &= 1.452 \text{ Method 1, page 11-10 in Lyman et al. (1982)} \\ a_s &= 9.35 \times 10^8 \text{ cm}^2/\text{mol Calculated from: } a_s = 8.45 \times 10^7 V_m^{2/3} \\ R &= 8.314 \times 10^7 \text{ erg/mol K} \\ \sigma_{WA} &= 72 \text{ dyne/cm Hoff et al. (1993)} \\ \sigma_{SA} &= 21.9 \text{ dyne/cm Value for acetaldehyde, Weast, 1980} \\ \sigma_{SW} &= 14.6 \text{ dyne/cm Average value for n-heptaldehyde and benzaldehyde, Girfalco} \\ &\quad \text{and Good, 1957} \\ k_{IW} &= 1.418 \times 10^{-7} \text{ cm}\end{aligned}$$

Formaldehyde emissions due to aerosols can now be calculated:

*Calculating the ratio of contaminant mass sorbed at the air-water interface to mass in gas volume of bubble:*

$$\frac{M_I}{M_b} = \frac{k_{IW}}{H_y(d_b/6)}$$

$$= 0.2138$$

*Calculating fraction of bubble interface ejected as aerosols:*

$$f_{IE} = \frac{R_A A d_b}{6 Q_G l_b}$$

$$= 4.35 \times 10^{-3}$$

where:

$$l_b = 5 \times 10^{-7} \text{ cm (Rosen, 1978)}$$

*Calculating formaldehyde mass transfer rate via aerosols from tank to the atmosphere:*

$$F_{y,a} = \frac{M_I}{M_b} f_{IE} F_{y,s}$$

$$= 0.00697 \text{ mg/min}$$

## **Volatilization from open tanks**

*Calculating molecular diffusion coefficient of formaldehyde in air:*

$$D_{y,\text{air}} = 4.09 \times 10^{-5} T^{1.9} (1/29 + 1/M)^{0.5} M^{-0.33} / P_t$$

$$= 0.174 \text{ cm}^2/\text{sec}$$

where:

$$\begin{aligned} T &= 298.15 \text{ K} \\ M &= 30.03 \text{ g/mol} \\ P_t &= 1 \text{ atm} \end{aligned}$$

*Calculating volatilization rate of formaldehyde from open tanks:*

$$\begin{aligned} F_{y,o} &= 2 c_{L,y} H_y A [D_{y,\text{air}} v_z / (pz)]^{0.5} \\ &= 13.8 \text{ mg/min} \end{aligned}$$

where:

$$\begin{aligned} D_{y,\text{air}} &= \text{molecular diffusion coefficient of chemical in air (l}^2/\text{t)} \\ V_z &= 0.508 \text{ m/sec} \\ z &= 0.48 \text{ m (shortest tank dimension gives highest mass transfer rate)} \end{aligned}$$

The gas side mass transfer coefficient ( $k_g$ ) in the above model is:

$$\begin{aligned} k_g &= 2[D_{y,\text{air}} v_z / (pz)]^{0.5} \\ &= 0.484 \text{ cm/sec} \end{aligned}$$

Thibodeaux (1979) reports a value of the liquid side mass transfer coefficient ( $k_l$ ) in large water bodies of about  $6 \times 10^{-4}$  cm/sec for wind speeds of 0.5 m/sec. Although not directly applicable to the current situation, it can be used as a first estimate to determine the potential for liquid film resistance to control the mass transfer rate.

$$\text{Liquid side resistance} = H_y / k_l = 3.3 \times 10^{-2} \text{ sec/cm}$$

$$\text{Gas side resistance} = 1/k_g = 2.1 \text{ sec/cm}$$

It can be concluded that formaldehyde volatilization from open tanks is controlled by gas-side mass transfer resistance; therefore, the CEBMPEA equation appears to be valid. It should be noted that it may be necessary to consider liquid-side mass transfer resistance for chemicals with larger Henry's constants. In this case the CEBMPEA model would not be valid.

Surprisingly, volatilization due to air sparging is less significant than that from open tanks. Although the concentration of formaldehyde in the bubbles is high (virtually at equilibrium with the formaldehyde concentration in the bath), the volume of air sparged is small compared to the volume of room air flowing over the top of the tanks.



### Concentration of formaldehyde in workplace air

$$\begin{aligned}C_y &= F_{y,T}/(V_R R_V k) \\&= 0.326 \text{ mg/m}^3 \\&= 0.265 \text{ ppmv}\end{aligned}$$

$$\begin{aligned}\text{where: } F_{y,T} &= 7.49 \text{ mg/min} + 0.421 \text{ mg/min} + 13.8 \text{ mg/min} = 21.71 \text{ mg/min} \\V_R &= 20 \text{ m} \cdot 20 \text{ m} \cdot 5 \text{ m} = 2000 \text{ m}^3 \\R_V &= 4 \text{ hr}^{-1} = 0.0667 \text{ min}^{-1} \\k &= 0.5\end{aligned}$$

### VII. COMPARISON OF PREDICTED FORMALDEHYDE CONCENTRATIONS IN WORKPLACE AIR TO MONITORING DATA

In this section, the concentrations of formaldehyde in the workplace air predicted by the model are compared to available monitoring data. The purpose of the comparison is not to validate the model but to determine if the modeling approach gives reasonable values of formaldehyde concentration. Model validation would require calculation of formaldehyde concentrations using the conditions specific to the monitoring sites. Such data are not available.

The results of an OSHA database (OCIS) search of monitoring data for formaldehyde (provided by OPPT) include 43 measured air concentrations for 10 facilities in Standard Industrial Classification (SIC) 3672 (printed circuit boards). The concentrations range from not detected to 4.65 ppmv. Most of the concentrations (37/42) range from  $\leq 0.04$  to 0.6 ppmv, with all but one less than 1.55 ppmv. Cooper et al. reports formaldehyde concentrations from three electroless plating operations measured over a two day period. The mean concentrations ranged from 0.088 to 0.199 ppmv. The predicted concentration of formaldehyde in the workplace air was 0.263 ppmv. Thus the predicted value is within the range of concentrations determined by monitoring, and less than the OSHA time-weighted-average concentration of 0.75 ppmv. The authors conclude that the results are reasonable.

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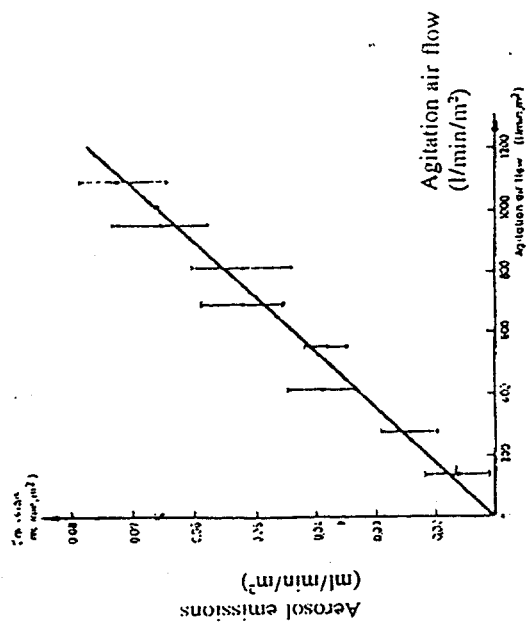


Figure 1a. Mist generation caused by air agitation.

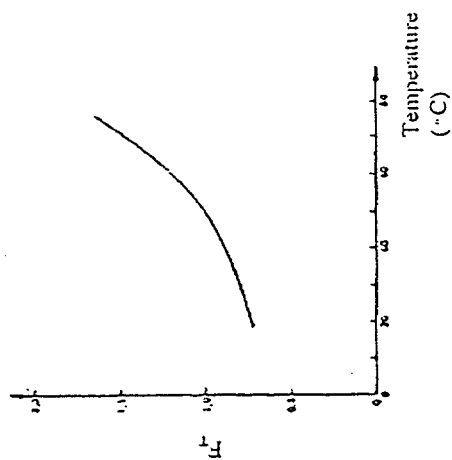


Figure 1b. Influence of bath temperature.

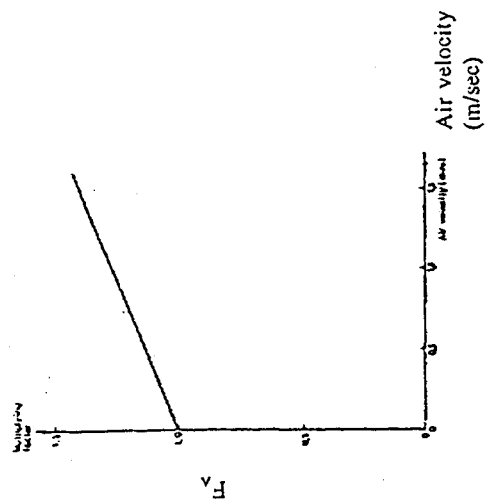


Figure 1c. Influence of air velocity across the bath surface.

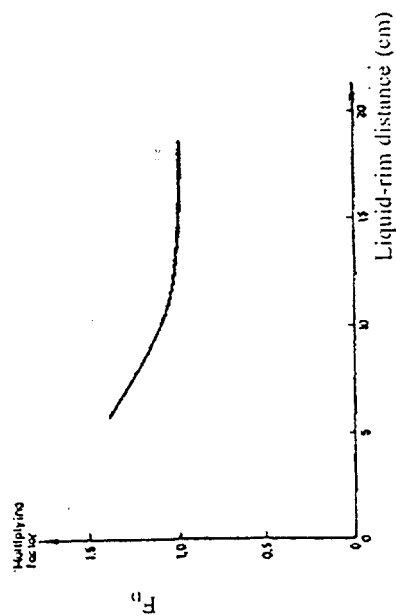


Figure 1d. Influence of the distance from the liquid to the bath rim.

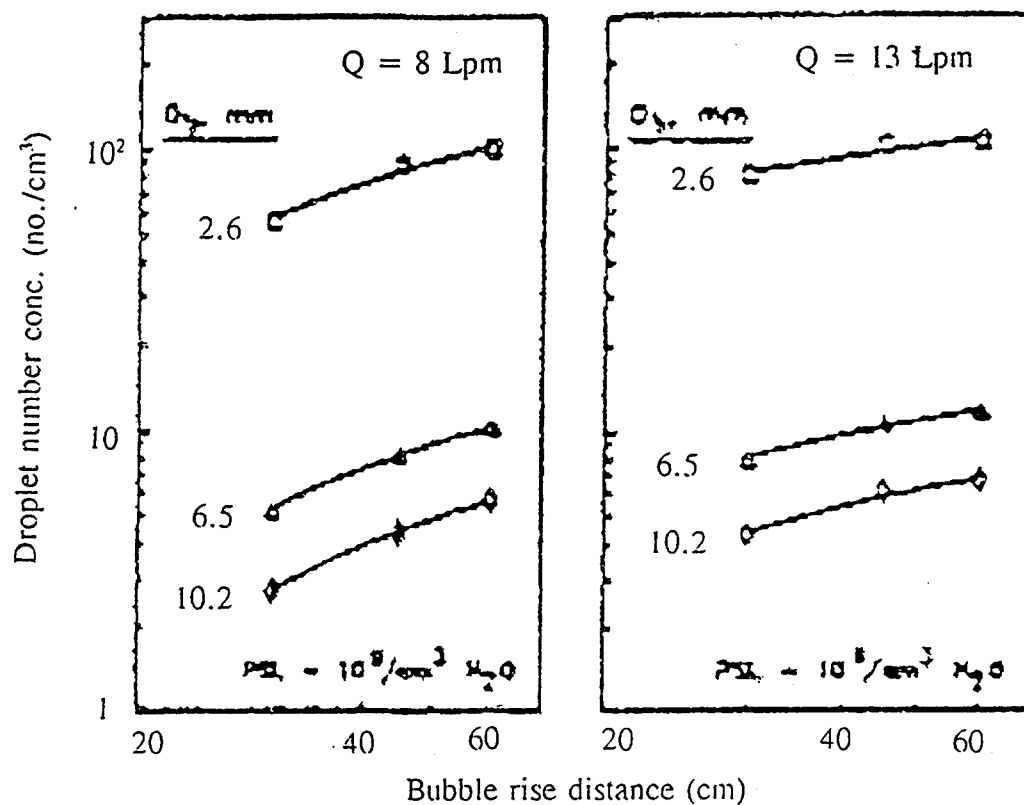


Figure 2. Effect of bubble rise distance on droplets number concentration. (From Wangwongwatana et al., 1990)